Palladium-Catalyzed Regio- and Stereoselective Carbothiolation of Terminal Alkynes with Azolyl Sulfides

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ABSTRACT: Palladium-catalyzed carbothiolation of terminal alkynes with azolyl sulfides affords various 2-(azolyl)alkenyl sulfides with perfect regio- and stereoselectivities. The present addition reaction proceeded through a direct cleavage of carbon–sulfur bonds in azolyl sulfides. The resulting adducts that are useful intermediates in organic synthesis are further transformed to multi-substituted olefins containing azolyl moieties.

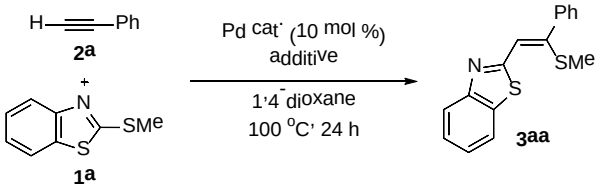
Carbothiolation of alkynes has been regarded as the most ideal approach to the highly substituted alkenyl sulfides in organic synthesis, which can generate carbon–carbon and carbon–sulfur bonds simultaneously.[1] Regio- and stereoselective addition of various carbon–sulfur bonds to alkynes has been achieved by using transition metal catalysts; thioesterification,[2] cyanothiolation,[3] allylthiolation,[4] alkenylthiolation,[5] acylthiolation,[6] iminothiolation,[7] alkynylthiolation,[8] and alkylthiolation.[9,10] Although only decarbonylative addition reaction of thioesters is known,[11] the atom-economical arylthiolation across alkynes has yet to be disclosed to date because carbon–sulfur bonds in aryl sulfides tend to cause a reversible oxidative addition.[12] While it was previously found that aryl sulfides underwent cross-coupling with organometallic reagents[13] probably because of the high reactivity of the once formed oxidative adducts for subsequent transmetalation, arylthiolation of alkynes is unprecedented.

Recently, Weller and Willis have reported rhodium-catalyzed addition of aryl sulfides bearing unique activating groups to terminal alkynes as a specific case.[14] On the other hand, addition reaction of heteroaryl sulfides to alkynes, which can construct the ubiquitous skeletons in pharmaceuticals and agrochemicals,[15] is significantly limited despite its utility. Although platinum-catalyzed furylthiolation,[11b,16] thienylthiolation,[17] and pyridylthiolation[18] of terminal alkynes with thioesters or with heteroaryl halides and arenethiolate salts are only known, those reactions produce toxic carbon monoxide or undesired by-products. We have recently disclosed the regio- and stereocontrolled chlorothiolation of alkynes with transition metal catalysts through the chlorine–sulfur bond cleavage of sulfenyl chlorides.[19] During the course of our research on selective addition of organosulfur compounds to alkynes, we investigated carbothiolation with a direct activation of heteroaryl sulfides. Herein, we report that a palladium complex ligated with *N*-heterocyclic carbene (NHC) catalyzed regio- and stereoselective addition of azolyl sulfides to terminal alkynes.

The reaction of 2-(methylthio)benzothiazole (**1a**) with phenylacethylene (**2a**) was carried out in 1,4-dioxane at 100 ºC for 24 h. The results employing various palladium catalysts are summarized in Table 1. In the presence of $Pd(PPh_3)_4$, the desired carbothiolation proceeded to yield the adduct **3aa** as a single product in 28% yield, while no reaction occurred without the catalyst (entry 1). The conventional palladium/phosphine catalytic systems were found to be less active (entries 2 and 3). Further screening of palladium catalysts revealed that Pd-PEPPSI-IPr ([1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridine)palladium(II) dichloride)[20] was the most effective (entry 4). Unexpectedly, the addition of a small amount of water improved the product yield (entry 5). The effect of water is unclear at this stage, but we presume that the *in-situ* formed LiOH from ^{n}BuLi and water might act as an efficient reductant of a palladium(II) precursor. This assumption was strongly supported by the reaction with $LiOH{\cdot}H_2O$, affording **3aa** in the comparable yield (entry 6). Among the additives examined, MeOH gave the best result (entry 7).[21] It is of note that the pre-

sent reaction was complete within 40 min under microwave irradiation at 140 °C (entry 8).

Table 1. Palladium-Catalyzed Addition of 2-(Methylthio)benzothiazole (1a) to Phenylacethylene (2a)[a]

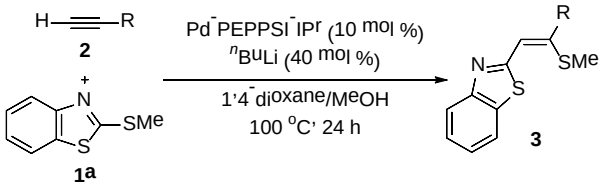


entry	Pd cat.	additive	yield (%)[b]
1	$Pd(PPh_3)_4$	none	28
2	$Pd(OAc)_2/PPh_3$ (1/4)	none	10
3	$Pd(dba)_2/PCy_3$ (1/2)	none	7
4	Pd-PEPPSI-IPr/^{n}BuLi (1/4)	none	75
5	Pd-PEPPSI-IPr/^{n}BuLi (1/4)	H_2O	89
6	Pd-PEPPSI-IPr/LiOH·H_2O (1/4)	none	84
7	Pd-PEPPSI-IPr/^{n}BuLi (1/4)	MeOH	95 (93)
8[c]	Pd-PEPPSI-IPr/^{n}BuLi (1/4)	MeOH	80

[a]Conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), Pd catalyst (0.10 mmol), ^{n}BuLi (0.40 mmol), additive (0.25 mL), in 1,4-dioxane (8.0 mL) at 100 °C for 24 h, unless otherwise stated. [b]NMR yields. An isolated yield is shown in parenthesis. [c]Microwave irradiation at 160 °C for 40 min.

With the optimized conditions in hand, various aromatic and aliphatic terminal alkynes **2** were examined for the reaction with **1a**, as shown in Table 2. The reaction of electron-rich arylacetylenes **2b** and **2c** proceeded smoothly to provide the corresponding adducts **3ab** and **3ac** in 81% and 91% yields, respectively (entries 1 and 2). In contrast, the reaction was slightly affected by a coordination ability of alkynes to a palladium center: carbothiolation of electron-poor or bulkier arylacetylenes **2d** and **2e** gave the products **3ad** and **3ae** in moderate yields (entries 3 and 4). In addition, internal alkynes such as diphenylacetylene and dimethyl acetylenedicarboxylate did not undergo the desired reaction, recovering the starting substrates quantitatively. Moreover, alkylacetylenes **2f** and **2g** were applicable to the reaction, providing **3af** and **3ag** in 67% and 70% yields, respectively (entries 5 and 6). The steric congestion of **2h** did not influence the efficiency of the reaction (entry 7). 3,3-Diethoxyl-1-propyne (**2i**) also reacted with **1a** to give **3ai** with the acetal moiety remained intact (entry 8). Furthermore, when an excess amount of diynes **2j** and **2k** on **1a** was employed, carbothiolation selectively occurred at one of two alkyne moieties to afford the 1:1 adducts **3aj** and **3ak**, albeit in low yields (entries 9 and 10).

Table 2. Palladium-Catalyzed Addition of 2-(Methylthio)benzothiazole (1a) to Terminal Alkynes 2[a]

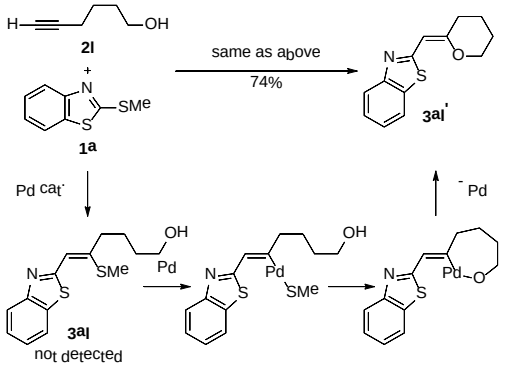


entry	R	2	3	yield (%)[b]
1	*p*-$MeOC_6H_4$	**2b**	**3ab**	81
2	*p*-MeC_6H_4	**2c**	**3ac**	91
3[c]	*p*-$CF_3C_6H_4$	**2d**	**3ad**	44
4[c]	1-Naphthyl	**2e**	**3ae**	50
5[c]	Hex	**2f**	**3af**	67
6[c]	^{n}Bu	**2g**	**3ag**	70
7	^{t}Bu	**2h**	**3ah**	60
8[c]	$CH(OEt)_2$	**2i**	**3ai**	75
9	*p*-(HC≡C)C_6H_4	**2j**	**3aj**	52
10	$HC{\equiv}C(CH_2)_3$	**2k**	**3ak**	30

[a]Reaction Conditions: **1a** (1.0 mmol), **2** (2.0 mmol), Pd-PEPPSI-IPr (0.10 mmol), ^{n}BuLi (0.40 mmol), in 1,4-dioxane (8.0 mL) and MeOH (0.125 mL) at 100 °C for 24 h. [b]Isolated yields. [c]Microwave irradiation at 160 °C for 40 min.

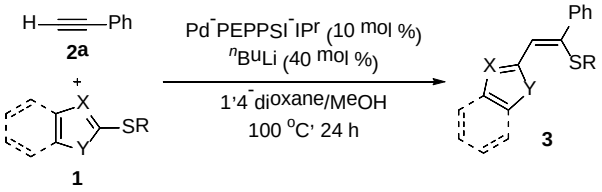
As a small variant of the terminal alkynes, 5-hexyn-1-ol (**2l**) was employed to the reaction of **1a** (Scheme 1). The expected carbothiolation adduct **3al** was not obtained, while carboetherification product **3al'** was obtained in 74% yield. After the formation of carbothiolation adduct **3al**, palladium-catalyzed etherification of alkenyl sulfide **3al** might give **3al'** through oxidative addition of **3al**, ligand exchange between thiolate and alkoxide, and reductive carbon–oxygen bond formation.[22] To the best of our knowledge, there are no reports on etherification of alkenyl sulfides with alcohols despite their seeming simplicity. The configuration of **3al'** was determined by NOESY analysis.[21]

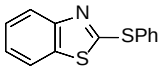
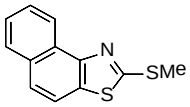
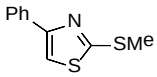
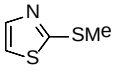
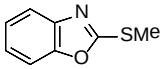
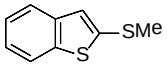
Scheme 1. Carbothiolation of 5-Hexyn-1-ol (2m) with 1a



Next, we explored the scope of heteroaryl sulfides **1** in the reaction with phenylacethylene (**2a**) (Table 3). The addition of 2-benzothiazolyl phenyl sulfide (**1b**) gave **3ba** as a sole product through chemoselective cleavage of C(2-benzothiazolyl)–S bond rather than C(phenyl)–S bond (entry 1). The stereochemistry of **3ba** was unambiguously determined by X-ray crystallographic analysis, which provides clear evidence of the regio- and stereoselective carbothiolation process (Figure 1).[23] In addition to naphthothiazolyl sulfide **1c**, thiazolyl sulfides **1d** and **1e** were also amenable to the reaction (entries 2–4). Carbothiolation adduct **3fa** was obtained from benzoxazolyl sulfide **1f**, while the reaction of benzothienyl sulfide **1g** gave the product **3ga** in 11% yield. It is of note that methyl 2-pyridyl sulfide and methyl phenyl sulfide did not undergo the reaction.

Table 3. Palladium-Catalyzed Addition of Azolyl Sulfides 1 to Phenylacethylene (2a)[a]



entry	heteroaryl sulfide	1	3	yield (%)[b]
1		**1b**	**3ba**	82
2		**1c**	**3ca**	75
3[c]		**1d**	**3da**	79
4[c]		**1e**	**3ea**	57
5[c]		**1f**	**3fa**	43
6		**1g**	**3ga**	11

[a]Conditions: **1** (1.0 mmol), **2a** (2.0 mmol), Pd-PEPPSI-IPr (0.10 mmol), [n]BuLi (0.40 mmol), in 1,4-dioxane (8.0 mL) and MeOH (0.125 mL) at 100 ºC for 24 h. [b]Isolated yields. [c]Microwave irradiation at 160 ºC for 40 min.

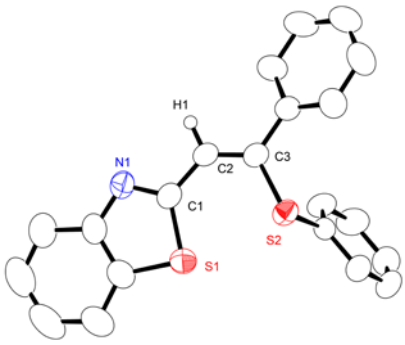
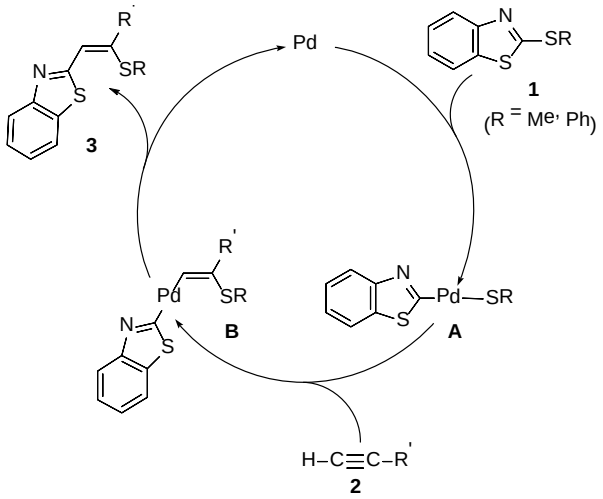


Figure 1. ORTEP drawing of 3ba determined by X-ray crystallography with 50% thermal ellipsoidal plotting.

A plausible reaction mechanism of the present carbothiolation is shown in Scheme 2. Oxidative addition of **1** to the palladium(0) species occurs to generate the (2-benzothiazolyl)palladium(II) thiolate **A**. A cleavage of C(heteroaryl)–S bond would undergo in preference to those of C(methyl)–S and C(phenyl)–S bonds, which would result from a favorable coordination of heteroatoms in **1** to a palladium center prior to oxidative addition.[12,13] The subsequent regio- and stereoselective insertion of terminal alkynes **2** into the palladium–sulfur bond affords alkenyl(2-benzothiazolyl)palladium(II) intermediate **B**. The regioselectivity can be rationalized as follows. During migratory insertion of **A** with terminal alkynes **2**, bulkier carbene-ligated palladium avoids a steric repulsion with the substituents of the alkyne **2**. The proposed mechanism is consistent to a precedent observation of the alkyne insertion to the metal–sulfur bond,[24] but an alternative pathway through carbopalladation of alkyne cannot be ruled out. Finally, reductive elimination proceeds to furnish **3**, regenerating the initial palladium complex.

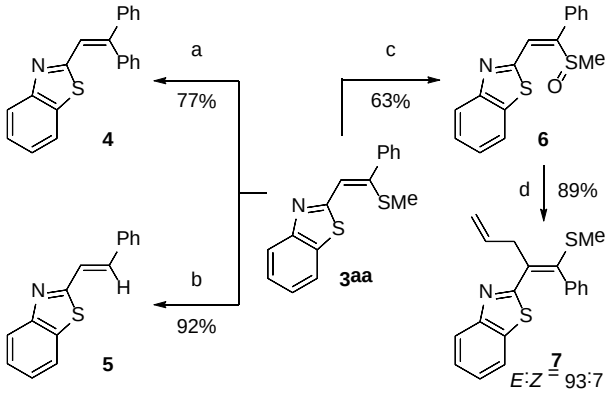
Scheme 2. A Plausible Reaction Mechanism



Synthetic utility of the carbothiolation adduct **3** was successfully demonstrated as shown in Scheme 3. Alkenyl methyl sulfide **3aa** can act as an alkenyl pseudohalide in cross-coupling: palladium-catalyzed Negishi coupling of

3aa with phenylzinc chloride occurred to give **4** in 77% yield.[13] Nickel-catalyzed reduction of **3aa** with zinc provided 2-(phenethyl)benzothiazole (**5**) in 92% yield.[25] Oxidation of **3aa** with *m*-chloroperbenzoic acid (*m*CPBA) proceeded with a retention of stereochemistry to afford the corresponding sulfoxide **6**. The configuration of **6** was confirmed by X-ray crystallographic analysis (Figure 2).[26] Pummerer-type reaction of alkenyl sulfoxide **6** with allyltrimethylsilane in the presence of Tf_2O and K_2CO_3 furnished the allylated product **7** in 89% yield with a high stereoselectivity.[9b,27,28] It is noteworthy that allylation proceeded with an inversion of configuration and the formation of (*E*)-isomer predominated, which was determined by NOESY analysis.[21]

Scheme 3. Transformations of 3aa.



Conditions a: Pd-PEPPSI-IPr (15 mol %), PhZnCl (3 equiv), THF, 60 °C, 3 h. b: $NiCl_2(dppf)_2$ (15 mol %), $ZnCl_2$ (2 equiv), Zn (2 equiv), THF, 66 °C, 58 h. c: *m*CPBA (1.2 equiv), CH_2Cl_2, 40 °C, 4.5 h. d: Tf_2O (2 equiv), K_2CO_3 (2 equiv), $CH_2{=}CHCH_2SiMe_3$ (3 equiv), $MeNO_2$, 25 °C, 2 h.

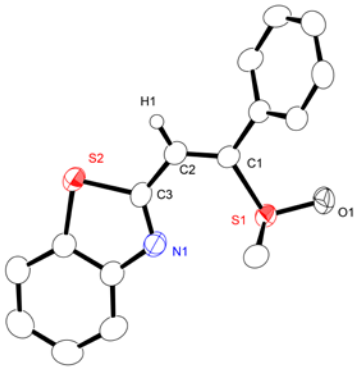


Figure 2. ORTEP drawing of 6 determined by X-ray crystallography with 50% thermal ellipsoidal plotting.

In summary, the palladium/NHC complex, Pd-PEPPSI-IPr, catalyzed addition of azolyl sulfides to terminal alkynes to afford (*Z*)-2-(azolyl)alkenyl sulfides with perfect regio- and stereoselectivities. The reaction proceeds with a direct cleavage of heteroaryl–sulfur bonds, which is widely applicable to substrates with various functionalities. The present method can be utilized for the construction of the highly functionalized olefin skeletons, which are often found in natural products and biologically active compounds.

ASSOCIATED CONTENT

Supporting Information

Details of all experiments procedures and spectroscopic data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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(23) Crystallographic data for the structure of 3ba have been deposited with The Cambridge Crystallographic Data Centre as the deposition number CCDC-1455018. This data can be obtained free of charge from on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223 336033 or www.ccdc.cam.ac.uk/data_request/cif.

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(28) Mechanism of regio- and stereoselective allylation is shown in the Supporting Information.

Authors are required to submit a graphic entry for the Table of Contents (TOC) that, in conjunction with the manuscript title, should give the reader a representative idea of one of the following: A key structure, reaction, equation, concept, or theorem, etc., that is discussed in the manuscript. Consult the journal's Instructions for Authors for TOC graphic specifications.